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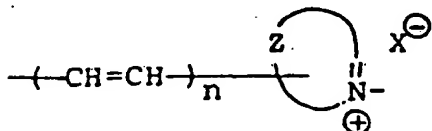
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(54) A contrast-enhancing agent for photolithography.

(57) A contrast-enhancing agent for photolithography which comprises:

(a) a photo-bleachable compound having, in its molecule, at least one characteristic structural unit represented by the general formula



In which Z is a divalent group which forms a heterocyclic aromatic ring structure with the nitrogen atom, X is a monovalent anionic group and n is a positive integer; and
(b) a water-soluble polymer as a binder.

The present invention relates to a contrast-enhancing agent for photolithography or, more particularly, to a composition used in photolithography for forming a patterned image of a photoresist layer by the light-projection method which enhances the contrast of the image by providing a thin layer of a photo-bleachable composition on the photoresist layer so as to make possible the formation of a patterned image of high resolution exceeding the highest resolution attainable in the prior art.

One effective method known in the prior art for enhancing the contrast of an image on a photoresist layer having a threshold value of contrast when the image is formed by light-projection through a photomask having lower contrast than the threshold value of contrast, the photoresist layer is overlaid with a thin layer containing a photo-bleachable compound. The photo-bleachable compound used in this process is a compound where the intensity of light absorption can be decreased by exposure to light in a wavelength region from ultraviolet to visible used for exposure (see, for example, Journal of Imaging Science, volume 30, No. 2, pages 65-68, March/April, 1986, by P.R. West, et al. and a preprint in Regional Technical Conference on "Photopolymers: Principles and Materials", November, 1982, by B.F. Griffing, et al.).

A particular method disclosed in Japanese Patent Kokai 59-106462 is to provide the photoresist layer with a thin layer of a contrast-enhancing agent comprising a polymeric binder and a photo-bleachable compound of which the ratio of the molar-extinction coefficient given in liter/g \cdot cm to the molecular weight is approximately 10 or higher in the unbleached condition and the ratio of the molar extinction coefficient in the unbleached condition to that in the bleached condition is approximately 10 or higher.

In this prior art method, the contrast-enhancing agent is prepared by dissolving an aryl nitron compound as a photo-bleachable compound and a polymeric binder in an organic solvent which may be an aliphatic or aromatic hydrocarbon solvent, halogenated aliphatic hydrocarbon solvent or alcohol. When such an organic solution is applied to the surface of the photoresist layer to form a contrast-enhancing layer, it is more or less unavoidable that the surface of the photoresist layer is attacked and at least partially dissolved by the organic solvent in the solution to cause intermixing of the contrast-enhancing agent and the photoresist composition at the interface of the layers so that the quality of the patterned image is greatly affected. In addition, the contrast-enhancing agent is hardly soluble in the developer solution of the photoresist layer so that the procedure of development must be preceded by dissolving and removing the contrast-enhancing layer with an organic solvent so that the process of development is necessarily complicated and troublesome.

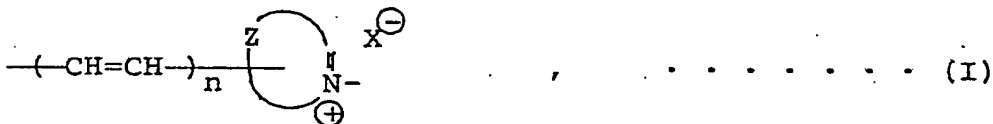
In order to provide a solution for the above mentioned problems in respect of the development procedure, improved contrast-enhancing agents have recently been disclosed in which the contrast-enhancing layer can be removed and the photoresist layer can be developed in one step. Some of such improved compositions include those disclosed in "Denshi Zairyou" (Electronic Materials), volume 46, No. 7 (1985) and in the lecture presented at the Allied Lectures related to Applied Physics, Japan, 1985, spring session, comprising a diazo compound as the photo-bleachable compound and pullulan as the binder and those disclosed in Nikkel New Materials, January 13 Issue, page 29 (1986) in which pullulan and poly(vinyl pyrrolidone) are combined as the binder.

These contrast-enhancing agents, however, are defective in respect of their long-term storage stability as a consequence of the formulation comprising a reactive diazo compound as the photo-bleachable compound.

It would be desirable, therefore, to provide a novel contrast-enhancing agent free from the above described problems and disadvantages in the conventional contrast-enhancing agents of prior art, which is characteristically advantageous in respect of its long-term storage stability as well as in respect of its solubility behavior so that the photoresist layer is not attacked by the agent when the contrast-enhancing layer is formed thereon and so that the development of the photoresist layer can be carried out without being preceded by the step of dissolving the contrast-enhancing layer.

The contrast-enhancing agent of the present invention comprises:

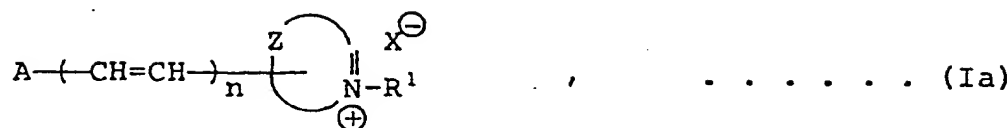
(a) a photo-bleachable compound having, in its molecule, at least one characteristic structural unit represented by the general formula



in which Z is a divalent group which forms a heterocyclic aromatic ring structure with the nitrogen atom, X is a monovalent anionic group and n is a positive integer; and

(b) a water-soluble polymer as a binder.

Preferably, the open bond at the left-hand end of the ethylenic linkage or linkages in the general formula (I) should be bonded to a substituted or unsubstituted aromatic group and the open bond of the nitrogen atom in the general formula (I) should be bonded to a hydrogen atom or a monovalent hydrocarbon group. Such a photo-bleachable compound is represented by the general formula



in which A is a substituted or unsubstituted monovalent aromatic hydrocarbon group and R¹ is a hydrogen atom or a monovalent hydrocarbon group which is an alkyl, alkenyl or aralkyl group, the other symbols each having the meaning defined above.

Preferably the photo-bleachable compound should have two structural units of the general formula (I) in its molecule.

The water-soluble polymer as the binder should preferably be used in an amount in the range from 0.5 to 10 parts by weight per part by weight of the photo-bleachable compound, component (a).

The present invention will now be described in more detail and with reference to the drawings in which: FIGURES 1, 2 and 3 each show the photo-bleaching characteristics of the contrast-enhancing agents prepared in Examples 1 and 2, in Examples 3 and 4, and in Examples 5 and 6, respectively.

FIGURE 4 illustrates photosensitivity characteristic curves obtained in Example 7.

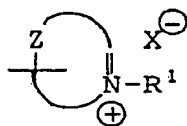
FIGURE 5 shows the photo-bleaching characteristics of the contrast-enhancing agent prepared in Example 9.

FIGURE 6 illustrates a photosensitivity characteristic curve obtained in Example 10.

The essential components in the inventive contrast-enhancing agent are the specific photo-bleachable compound having, in its molecule, at least one nitrogen-containing heterocyclic structural unit of the general formula (I) as the component (a) and a water-soluble polymeric binder as the component (b). The photo-bleachable compound as the component (a) is preferably a compound represented by the general formula (Ia) given above. In this general formula, the group denoted by A is a substituted or unsubstituted aromatic group.

Phenyl, naphthyl, furyl, pyrrolyl, thienyl, benzofuryl, benzothienyl, indolyl, pyridyl and quinolyl groups are examples of unsubstituted aromatic groups. When the group denoted by A is a substituted aromatic group, the substituent can be any atom or group capable of substituting on the aromatic nucleus including halogen atoms hydroxy, alkyl, alkoxy, amino, substituted amino, formyl, alkoxycarbonyl, acyl and methylene dioxy groups.

The heterocyclic aromatic structure of the formula



in the general formula (Ia) without the portion of $A-(CH=CH)_n-$ can be derived from one of the compounds represented by the following general formulas:

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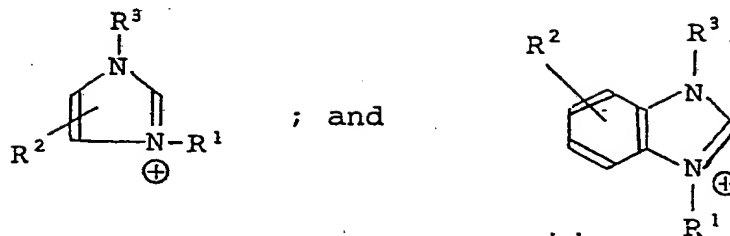
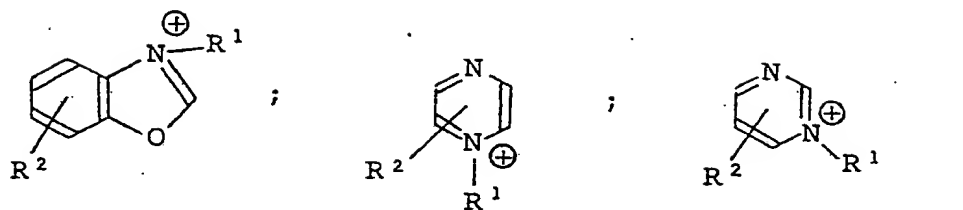
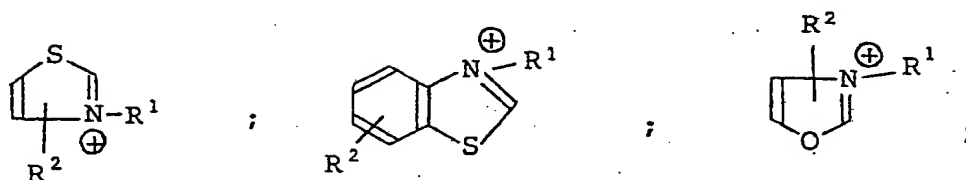
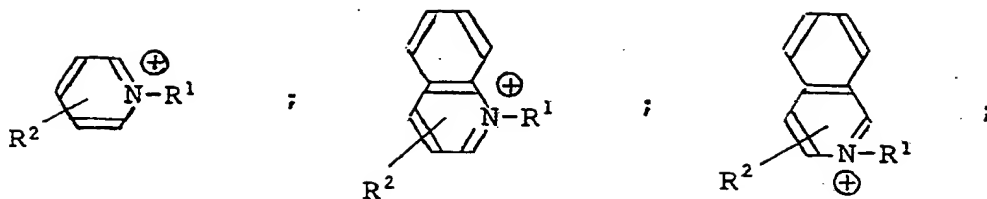
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In these formulas, the symbols R^1 and R^3 are each a hydrogen atom or a monovalent hydrocarbon group selected from alkyl, alkenyl and aralkyl groups while these alkyl, alkenyl and aralkyl groups may optionally be

substituted by or contain at least one group or linkage selected from hydroxy group, carbamoyl group and ether linkage and the aralkyl groups may contain one or more ethylenically unsaturated linkages. The symbol R^2 in the formulas denotes a hydrogen or halogen atom or an alkyl, alkoxy or alkoxy carbonyl group.

Further, the symbol X in the general formula (I) or (Ia) represents a monovalent anionic group such as halide, alkyl sulfate, dihydrogen phosphate ($H_2PO_4^-$), sulfonate, and hydrogen sulphate (HSO_4^-).

Optionally two or more kinds of these photo-bleachable compounds may be used in combination in the inventive contrast-enhancing agent.

The subscript n in the general formula (I) or (Ia) is a positive integer and, although the value of n has no particular upper limit, it is preferable that n has a value of 1, 2 or 3 or, more preferably, 1 or 2 so that preferable photo-bleachable compounds are represented by the following general formula (II) or (III):

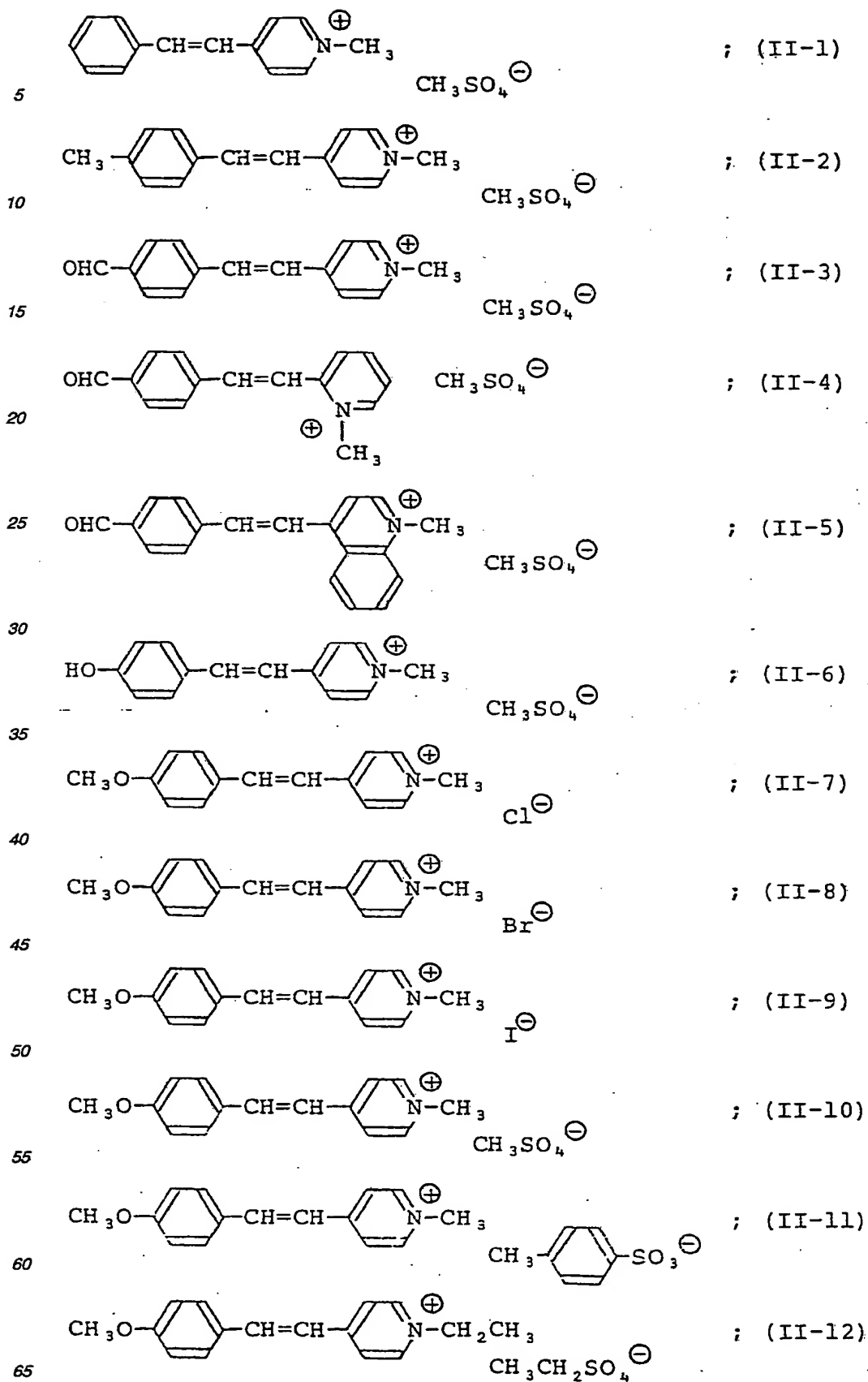


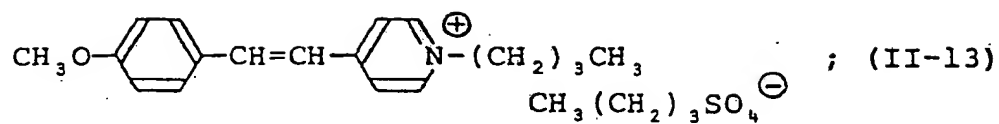
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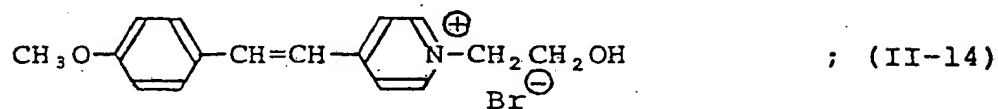
in which the symbols A, Z, R^1 and X each have the same meaning as defined above.

Particular examples of the photo-bleachable compounds in conformity with the general formula (II) include the compounds expressed by the following structural formulas (II-1) to (II-53) and those in conformity with the general formula (III) include the compounds expressed by the following structural formulas (III-1) to (III-4):

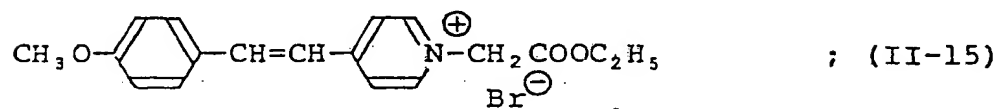




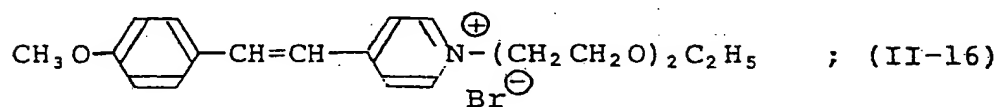
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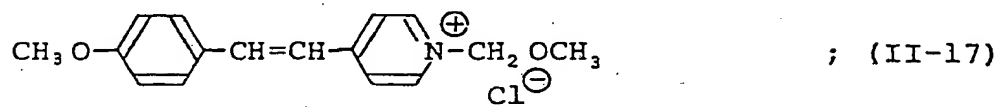
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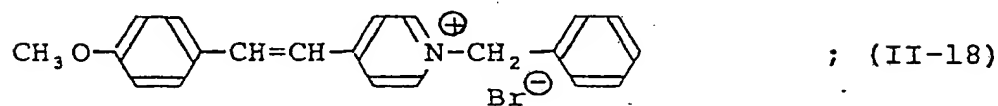
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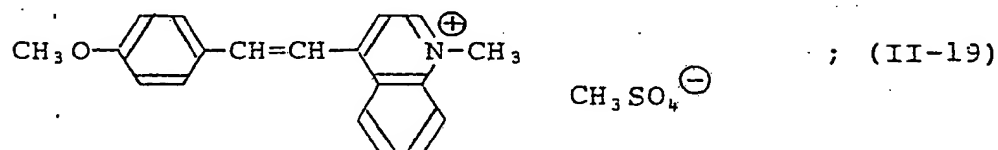
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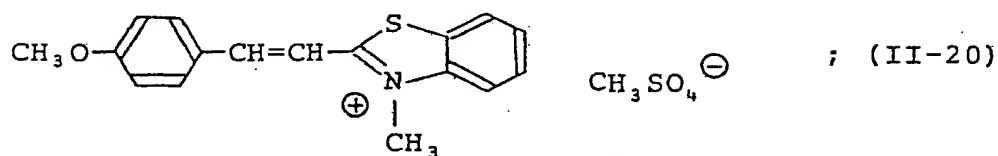
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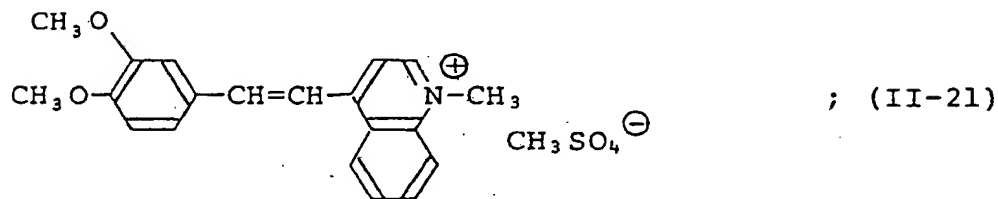


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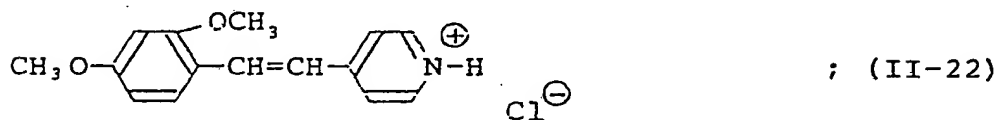


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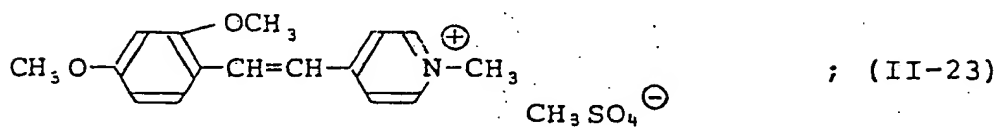
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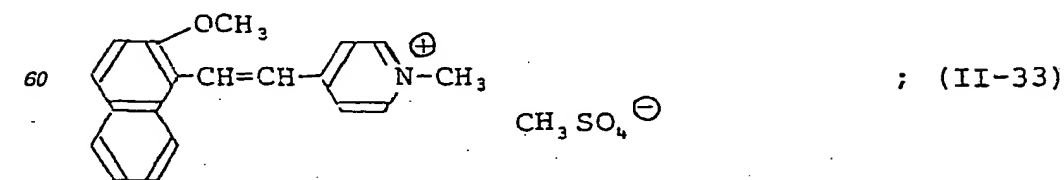
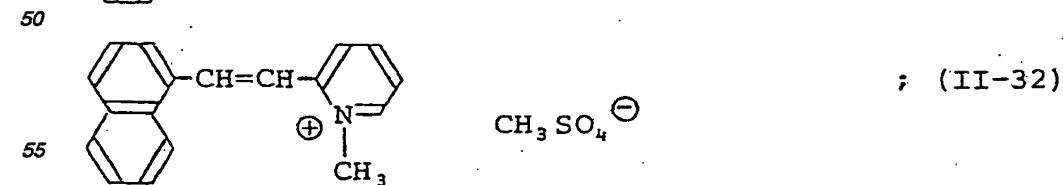
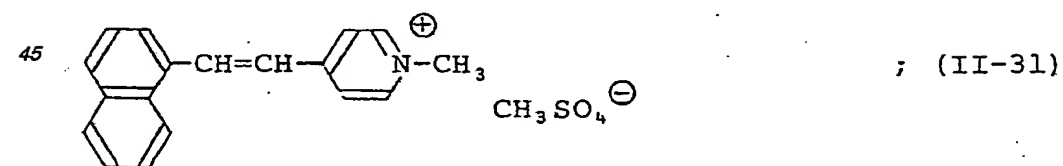
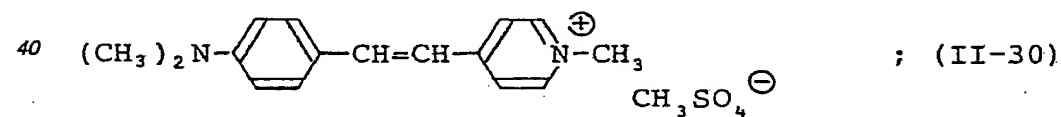
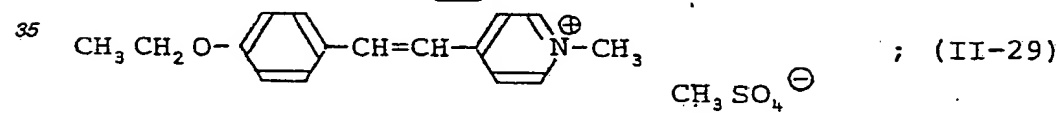
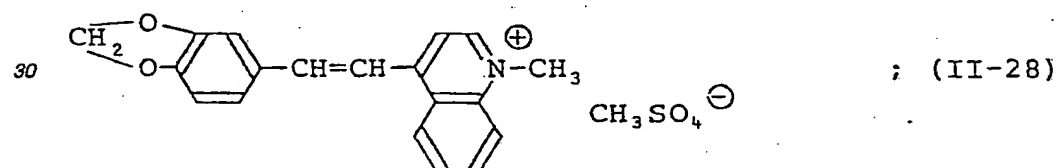
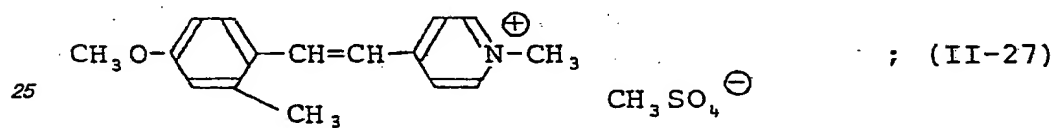
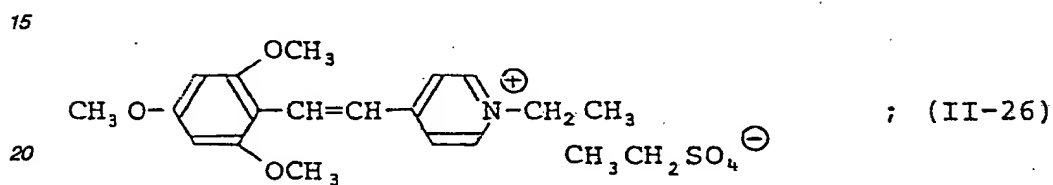
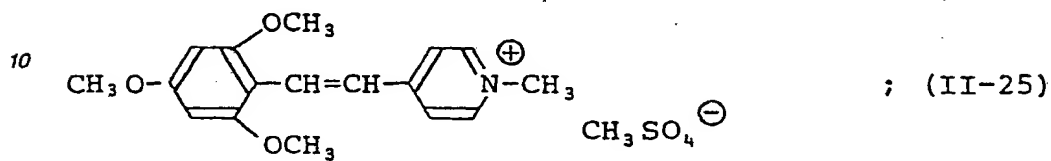
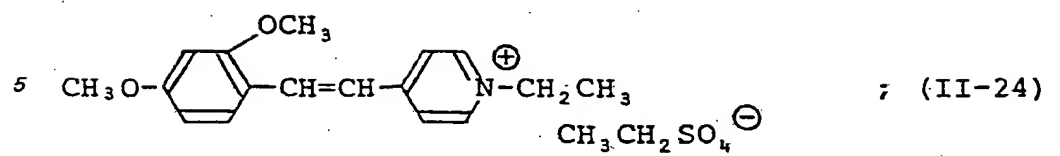


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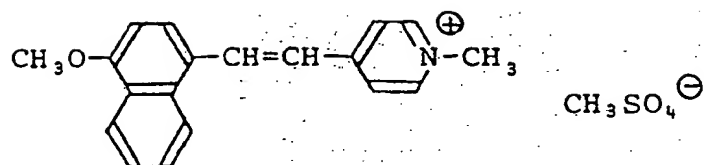


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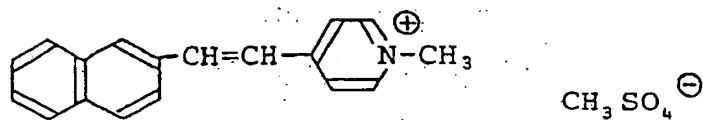


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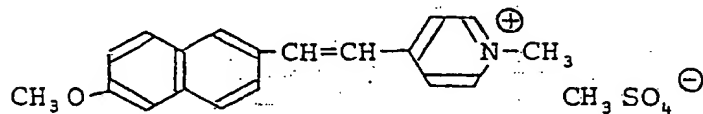
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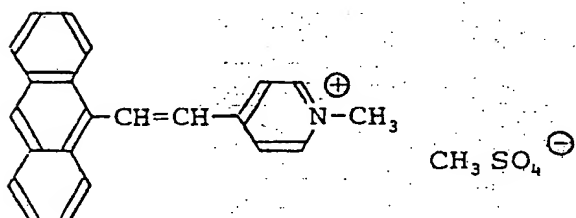
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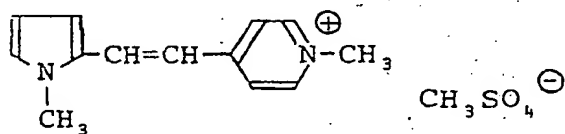
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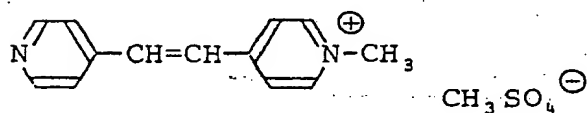
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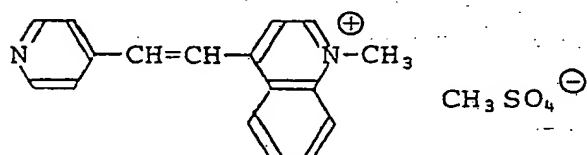
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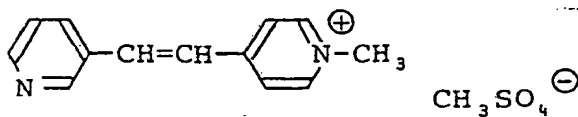
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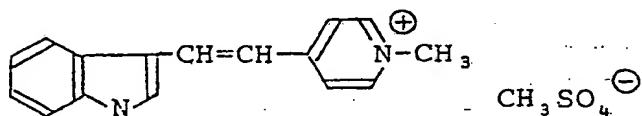
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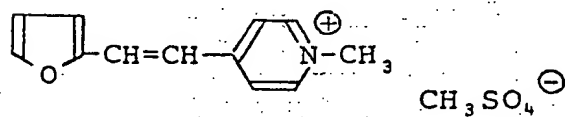
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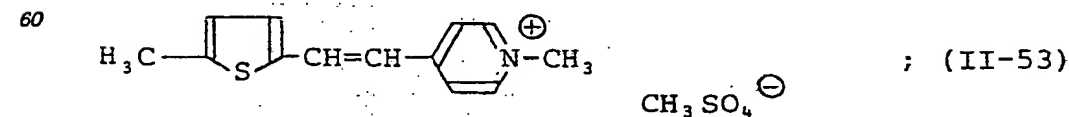
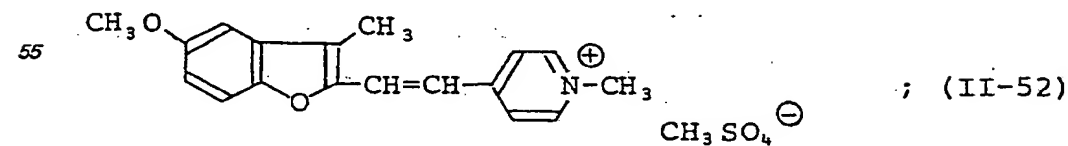
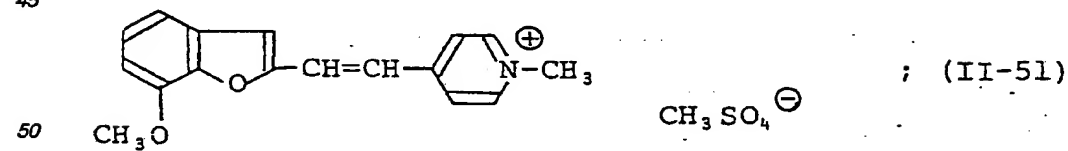
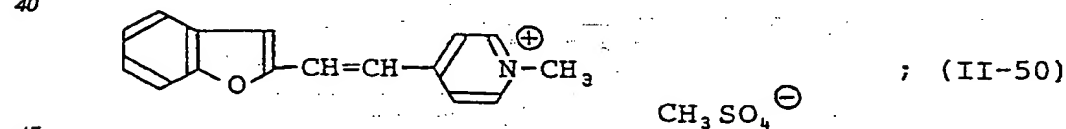
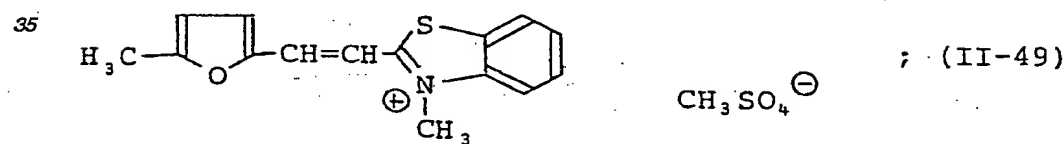
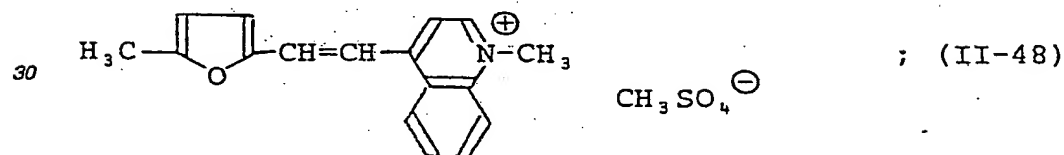
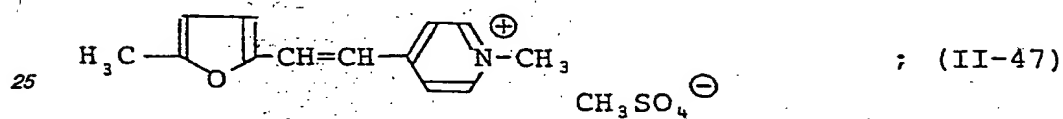
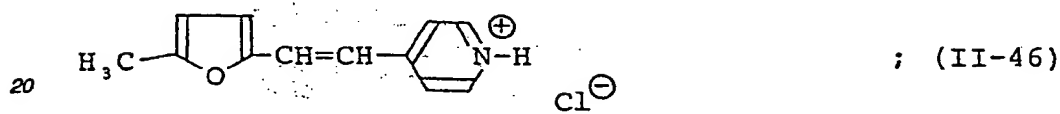
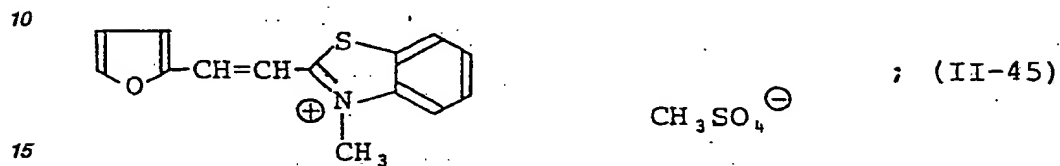
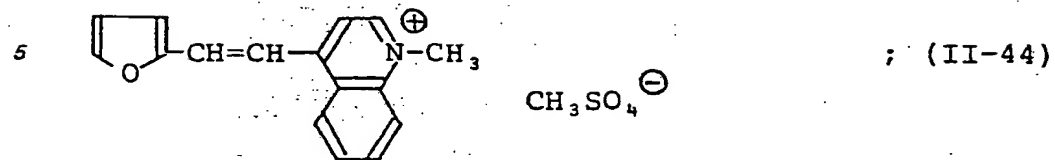
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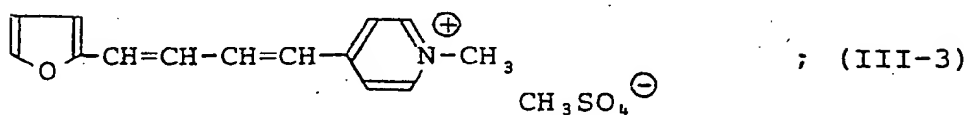
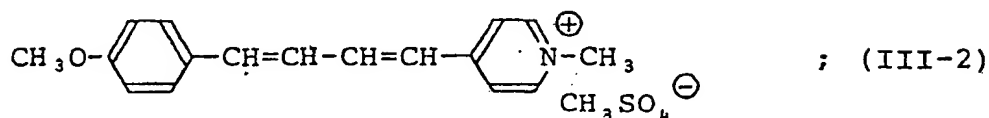
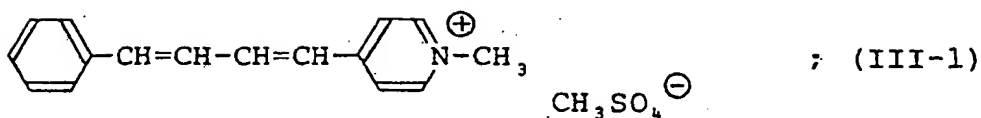
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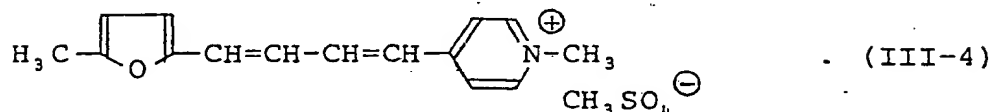
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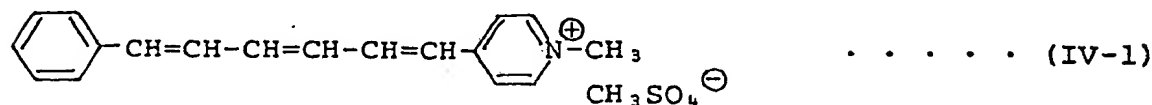
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and



An example of the photo-bleachable compound of the general formula (Ia) in which the subscript n is 3 is the compound expressed by the following structural formula (IV-1):



The photo-bleachable compound represented by the general formula (Ia) can be synthesized by various known methods, of which a preferable synthetic route.

Thus, a heterocyclic nitrogen-containing aromatic compound having a methyl group bonded to the aromatic ring and a quaternary salt-forming compound of the formula $\text{R}^1\text{-X}$, in which R^1 and X each have the same meaning as defined above, are reacted in a suitable organic solvent such as an alcohol, e.g. methyl alcohol, isopropyl alcohol or, ethylene glycol, monomethyl ether, dimethylformamide, or demethylacetamide to form a quaternary salt of the heterocyclic compound which is then reacted with an aromatic aldehyde compound of the formula $\text{A}-(\text{CH}=\text{CH})_n\text{-CHO}$, in which A has the same meaning as defined above and n is zero or a positive integer, in a suitable solvent, which may be the same one as used in the preceding step, in the presence of a catalyst to give the compound represented by the general formula (Ia).

An alternative synthetic route is to first perform the reaction between the heterocyclic nitrogen-containing aromatic compound having a methyl group bonded to the aromatic ring and the aromatic aldehyde compound of the formula $\text{A}-(\text{CH}=\text{CH})_n\text{-CHO}$ and the product of this first step reaction is then reacted with the quaternary salt-forming compound of the formula $\text{R}^1\text{-X}$.

Exemplary of the aromatic aldehyde compound of the formula $\text{A}-(\text{CH}=\text{CH})_n\text{-CHO}$ used as one of the reactants in the above mentioned reactions are: benzaldehyde; 4-tolylaldehyde; terephthalaldehyde; 4-hydroxybenzaldehyde; 4-methoxybenzaldehyde, i.e. p-anisaldehyde; 4-chlorobenzaldehyde; 3,4-dimethoxybenzaldehyde, i.e. veratraldehyde; 2,4-dimethoxybenzaldehyde; 2,4,6-trimethoxybenzaldehyde; 2-methyl-4-methoxybenzaldehyde; 3-methoxy-4-(2'-dimethoxy) benzaldehyde; 3,4-dioxymethylene benzaldehyde; 4-ethoxybenzaldehyde; 4-dimethylaminobenzaldehyde; α -naphthaldehyde; 2-methoxy-1-naphthaldehyde; 4-methoxy-1-naphthaldehyde; β -naphthaldehyde; 6-methoxy-2-naphthaldehyde; 9-anthranylaldehyde; N-methylpyrrol-2-aldehyde; 4-pyridylaldehyde; 3-pyridylaldehyde; 3-indolylaldehyde; furfural; 5-methylfurfural; 2-benzofurylaldehyde; 7-methoxy-2-benzofurylaldehyde; 3-methyl-5-methoxy-2-benzofurylaldehyde; 2-thienylaldehyde; 5-methyl-2-thienylaldehyde; cinnamaldehyde; 4-methoxycinnamaldehyde; 3-(2-furyl)acryl aldehyde

hyde; 3-(5-methyl-2-furyl)acryl aldehyde; and 4-phenylbutadiene-1-aldehyde.

The heterocyclic nitrogen-containing aromatic compound having a methyl group bonded to the aromatic ring used in the reactions is exemplified by α - and γ -picolines, 2-methylquinoline, 4-methylquinoline, and 2-methylbenzothiazole. The quaternary salt-forming compound of the formula R^1-X is exemplified by dimethyl sulfate, diethyl sulfate, dipropyl sulfate, dibutyl sulfate, methyl halides, methyl p-toluenesulfonate, 2-hydroxyethyl halides, ethyl halogenoacetates, 2-halogenoethyl 2'-ethoxyethyl ethers, methoxymethyl halides, benzyl halides, and hydrogen halides. The halogen in the above named halogenated compounds may be chlorine, bromine or iodine.

The above described compounds represented by the general formula (Ia) are very effective as photo-bleachable compounds with a very large ratio of the molar extinction coefficient in the unbleached condition to the molecular weight and a large ratio of the molar extinction coefficient in the unbleached condition to that in the bleached condition. Therefore, the contrast-enhancing agent of the invention comprising such a compound is useful for imparting a greatly enhanced contrast to the patterned image formed on a photoresist layer by the projection of light when the contrast of the projected image is lower than the threshold value of contrast of the photoresist as a result of the increase in the space frequency of the image.

The above described photo-bleachable compounds each have absorption of light in a different wavelength region from the others so that the compound should be properly selected depending on the kind of the light source, which may emit the g-lines, h-lines or i-lines, used in the exposure of the photoresist to light. Table 1 below shows the wavelength of maximum absorption, molar extinction coefficient at the wavelength and the ratio of the molar extinction coefficient given in liter/cm \cdot mole to the molecular weight for each of the photo-bleachable compounds expressed by the structural formulas (II-1) to (II-53), (III-1) to (III-4) and (IV-1) given above.

T a b l e 1

Compound No.	λ_{\max} , nm	Molar extinction coefficient ϵ , liter/cm · mole	Ratio of ϵ to molecular weight
II-1	342	34,100	110
II-2	354	36,200	113
II-3	343	45,800	137
II-4	328	37,100	111
II-5	376	29,600	77
II-6	374	34,000	105
II-7	373	26,900	103
II-8	373	29,000	95
II-9	372	30,800	87
II-10	373	34,600	103
II-11	385	36,400	92
II-12	379	36,500	100
II-13	373	33,900	80
II-14	373	28,300	84
II-15	373	33,300	88
II-16	372	40,000	98
II-17	375	31,100	107
II-18	373	36,200	95
II-19	412	29,700	77
II-20	402	38,000	105
II-21	419	27,700	67
II-22	387	28,000	101
II-23	393	30,900	84
II-24	393	29,500	75
II-25	402	33,400	84
II-26	402	34,300	81
II-27	394	26,600	69
II-28	422	26,900	67
II-29	373	34,300	98
II-30	448	25,700	73
II-31	376	20,600	58
II-32	364	15,200	42

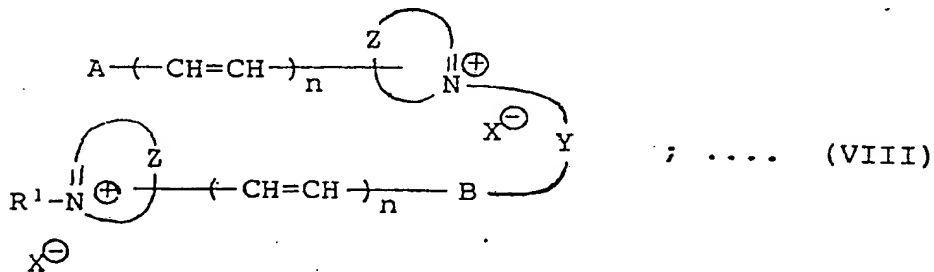
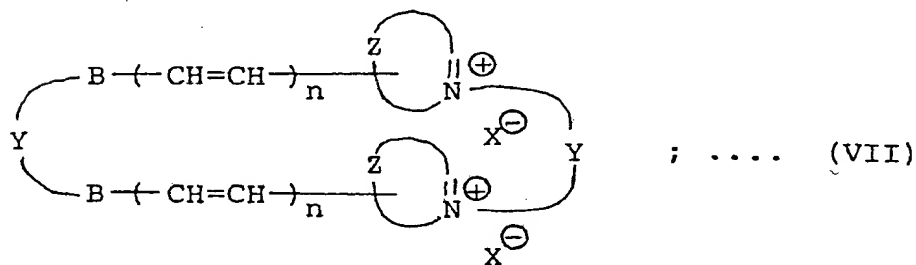
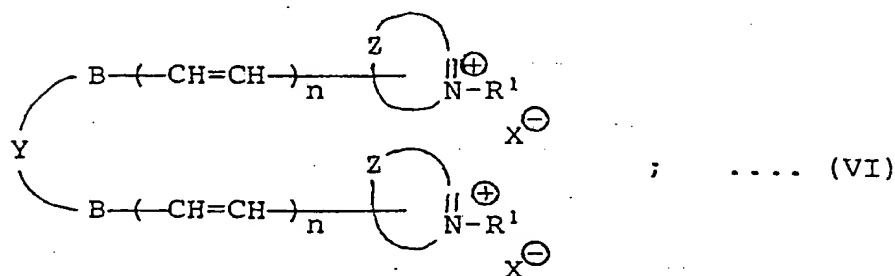
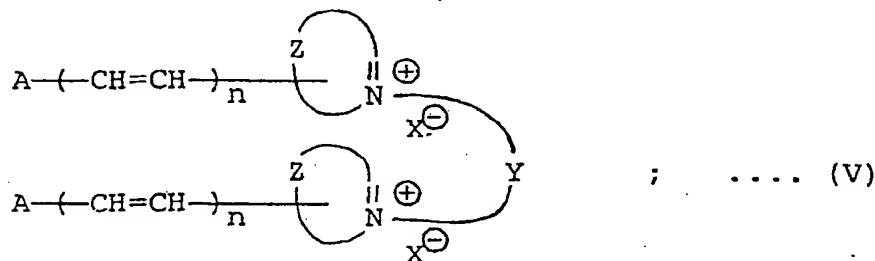
5	II-33	404	17,200	44
	II-34	409	25,000	65
	II-35	353	31,900	89
10	II-36	388	31,700	82
	II-37	430	10,100	25
	II-38	425	32,400	104
15	II-39	314	34,200	111
	II-40	333	19,900	55
	II-41	325	31,900	103
20	II-42	418	34,900	101
	II-43	378	31,600	106
	II-44	417	30,800	88
25	II-45	404	40,000	113
	II-46	392	39,400	178
	II-47	398	34,100	109
30	II-48	443	30,700	84
	II-49	428	41,500	113
	II-50	388	38,700	114
35	II-51	394	32,600	87
	II-52	407	40,900	105
40	II-53	393	33,400	102
	III-1	377	45,800	137
45	III-2	402	39,300	108
	III-3	406	37,300	115
	III-4	425	37,000	110
50	IV-1	406	43,300	120

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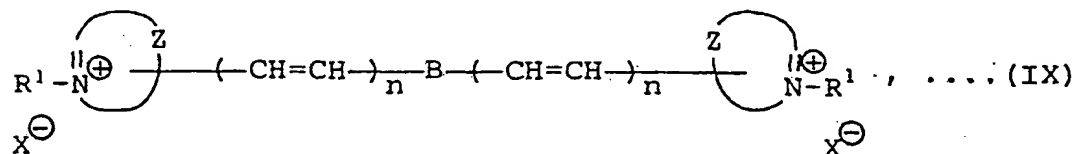
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65 While each of the above described photo-bleachable compounds has only one of the structural unit represented by the general formula (I) in a molecule, the photo-bleachable compounds belonging to another

preferable class have two structural units of the general formula (I). Such compounds can be classified into several classes depending on the manner by which the two structural units of the general formula (I) are combined together in a molecule. The compounds belonging to each class are represented by one of the following general formulas (V), (VI), (VII), (VIII) and (IX):



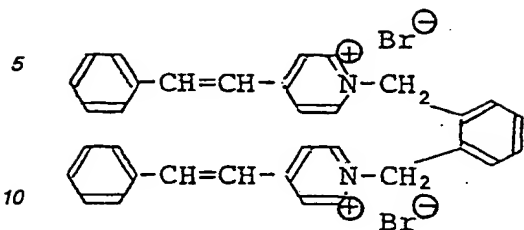
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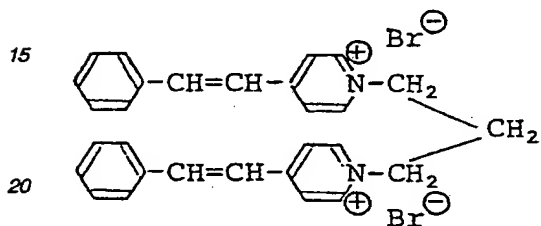
in which A, Z, R¹, X and n each have the same meaning as defined for the general formula (Ia), Y is a divalent organic group, B is a substituted or unsubstituted divalent aromatic group and, when a formula has two of the same symbols, they can be the same ones or may be different each from the other.

Exemplary of the particular compounds represented by the above given general formulas (V) to (IX) are those expressed by the following structural formulas (V-1) to (V-11), (VI-1) to (VI-3), (VII-1), (VIII-1) and (VIII-2)

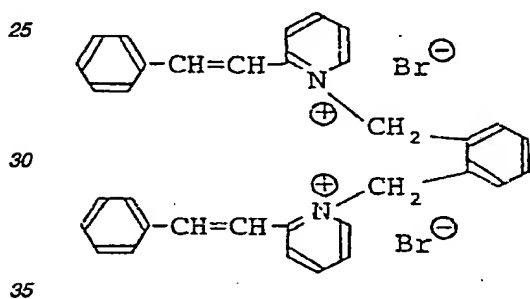
and (IX-1) and (IX-2):



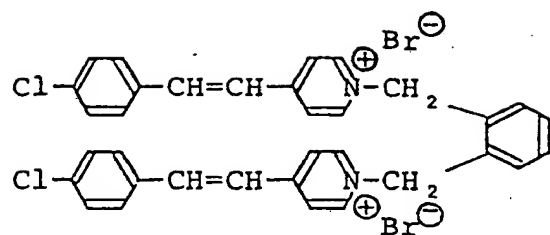
; (V-1)



; (V-2)

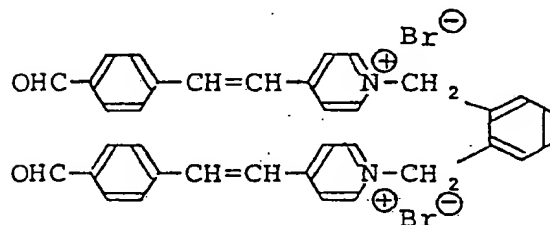


; (V-3)



; (V-4)

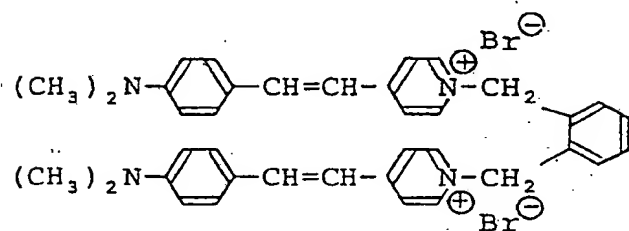
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; (V-5)

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15

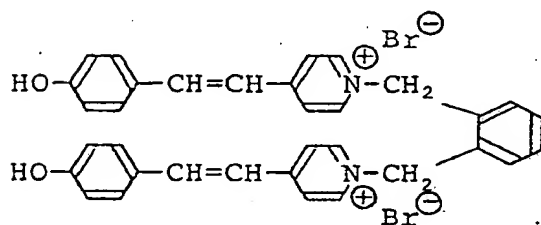


; (V-6)

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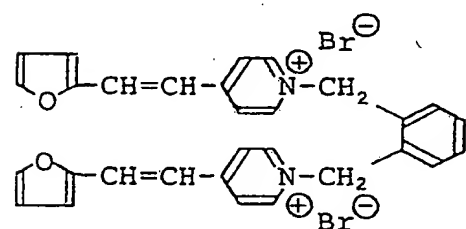
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; (V-7)

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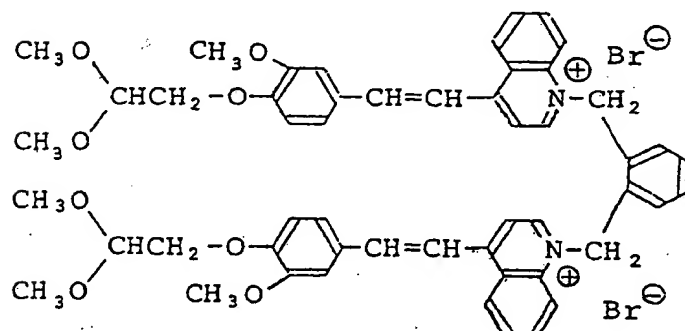
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; (V-8)

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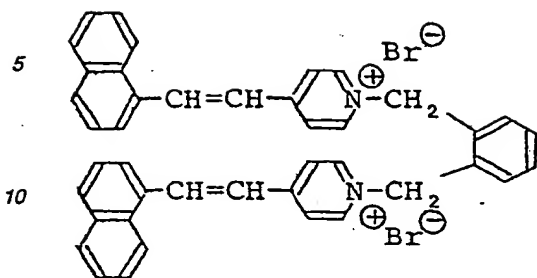


; (V-9)

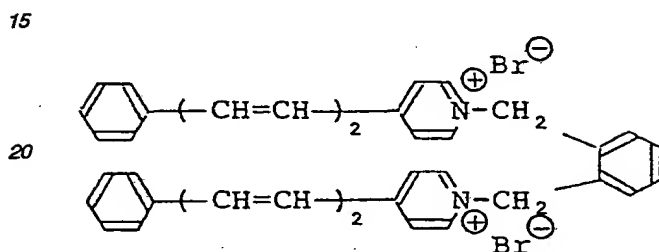
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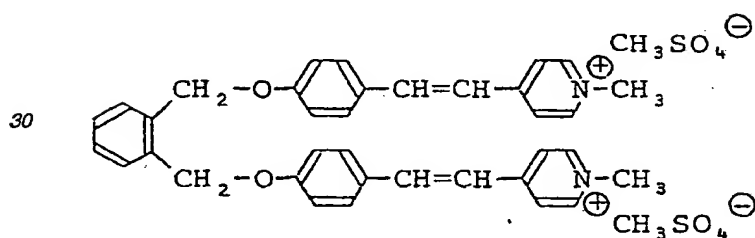
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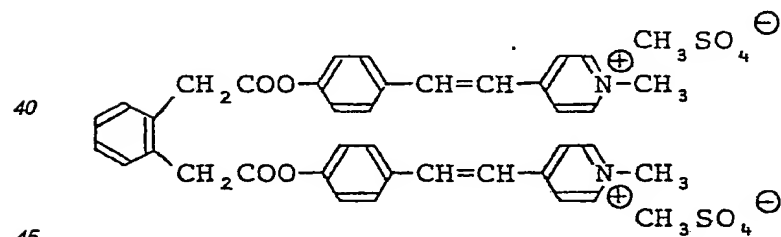
; (V-10)



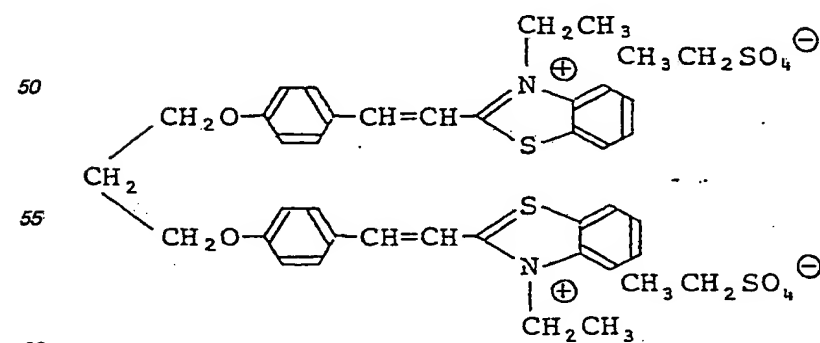
; (V-11)



; (VI-1)

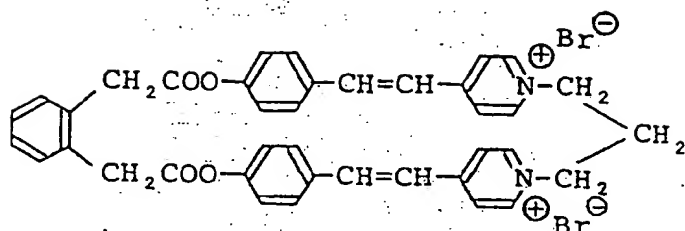


; (VI-2)

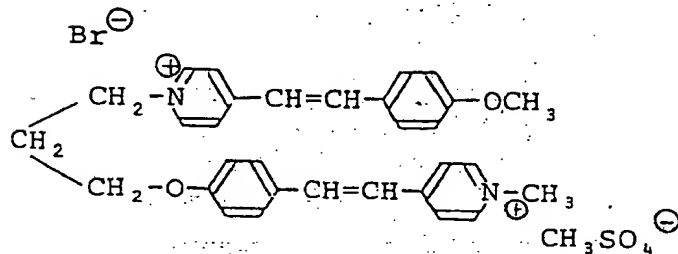


; (VI-3)

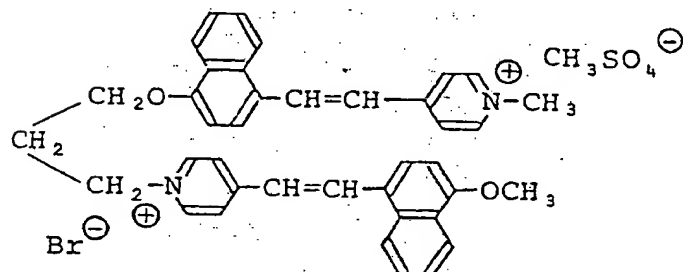
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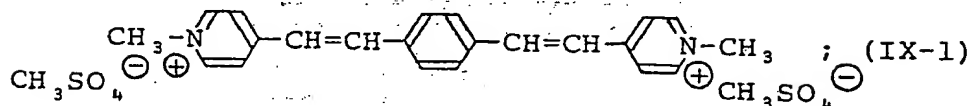
; (VII-1)



; (VIII-1)

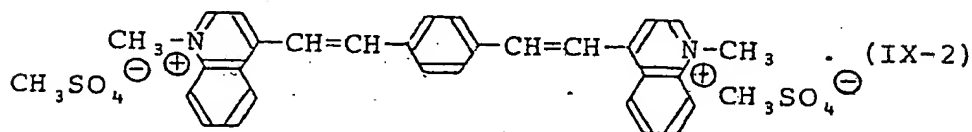


; (VIII-2)



; (IX-1)

and



. (IX-2)

The compounds represented by the general formula (V) given above can be synthesized, for example, by the following synthetic route. Thus, a nitrogen-containing heterocyclic aromatic compound having a methyl group

bonded to the aromatic nucleus is first reacted with a quaternary salt-forming compound of the formula X-Y-X, in which each symbol has the same meaning as defined above, in a suitable solvent such as an alcohol, e.g. methyl alcohol, isopropyl alcohol or ethylene glycol monomethyl ether, dimethylformamide, or dimethylacetamide to form a quaternary salt of the heterocyclic compound in which two molecules thereof are bonded together through the group Y as a linking unit, which is then reacted with an aromatic aldehyde compound of the general formula $A-(CH=CH)_n-CHO$ defined above in a suitable organic solvent in the presence of a catalyst.

The compounds represented by the general formula (VI) given above can be synthesized, for example, by the following synthetic route. Thus, a nitrogen-containing heterocyclic aromatic compound having a methyl group bonded to the aromatic nucleus is first reacted with an aromatic aldehyde compound and the reaction product is then reacted (1) with a difunctional organic compound which can be derived into the group denoted by Y after reaction followed by conversion of the reaction product into a quaternary salt by the reaction with a quaternary salt-forming compound of the formula R^1X , in which each symbol has the same meaning as defined above, or, alternatively, (2) with the quaternary salt-forming compound R^1X to be converted into a quaternary salt which is then reacted with the difunctional organic compound capable of being derived into the group denoted by Y after reaction.

The compounds represented by the general formula (VII) given above can be synthesized, for example, in the same synthetic route as in the preparation of the compounds represented by the general formula (VI) excepting replacement of the quaternary salt-forming compound R^1X with a compound represented by the general formula X-Y-X, in which each symbol has the same meaning as defined above.

The compounds represented by the general formula (VIII) or, in particular, the compound expressed by the formula (VIII-1) can be prepared in the following manner, for example. An alkali metal salt of 4-hydroxybenzaldehyde is reacted in a suitable organic solvent, e.g. an alcohol, dimethylformamide or dimethylacetamide, with 1,3-dibromopropane to form a monoether compound which is then reacted in an organic solvent such as dimethylformamide with stilbazole obtained from 4-methoxybenzaldehyde and γ -picoline followed by the reaction with a quaternary salt of γ -picoline obtained from γ -picoline and dimethyl sulfate.

The compounds represented by the general formula (IX) can be synthesized, for example, in the following manner.

The nitrogen-containing heterocyclic aromatic compound having a methyl group bonded to the aromatic nucleus is first reacted in a suitable organic solvent, which may be the same one as in the preparation of the compound of the general formula (V), with the quaternary salt-forming compound of the formula R^1X to form a quaternary salt thereof which is then reacted with an aromatic dialdehyde compound of the general formula $OHC-(CH=CH)_n-B-(CH=CH)_n-CHO$ in the presence of a catalyst.

The aromatic aldehyde compound used in the above described reaction may be the same one as in the preparation of the compounds represented by the general formula (Ia). The nitrogen-containing heterocyclic aromatic compound having a methyl group bonded to the aromatic nucleus also may be the same one as used in the preparation of the compounds represented by the general formula (Ia). The quaternary salt-forming compounds include, in addition to those given as the examples of the quaternary salt-forming compound used in the preparation of the general formula (Ia), 1,4-xylylene dihalides, and 1,3-dihalogopropanes.

The difunctional organic compound which can be derived into the group denoted by Y after reaction is exemplified by 1,2-xylylene dichloride and dibromide, benzene-1,2-diacetic acid dichloride and dibromide, 1,3-dichloro- and 1,3-dibromopropanes.

Table 2 below gives the wavelength of the maximum absorption, the molar extinction coefficient at the wavelength and the ratio of the molar extinction coefficient given in liter/cm • mole to the molecular weight of each of the compounds expressed by the formulas (V-1) to (V-11), (VI-1) to (VI-3), (VII-1), (VIII-1), (VIII-2), (IX-1) and (IX-2).

T a b l e 2

Compound No.	λ_{\max} , nm	Molar extinction coefficient ϵ , liter/cm · mole	Ratio of ϵ to molecular weight
V-1	346	69,500	111
V-2	348	68,900	119
V-3	342	44,400	71
V-4	354	76,800	110
V-5	343	93,400	137
V-6	447	51,500	73
V-7	383	67,600	103
V-8	379	58,400	96
V-9	416	54,600	56
V-10	400	35,000	49
V-11	384	61,900	91
VI-1	372	67,100	90
VI-2	339	70,600	88
VI-3	394	82,600	97
VII-1	345	71,000	98
VIII-1	363	61,000	93
VIII-2	400	47,000	69
IX-1	393	71,000	132
IX-2	430	58,900	93

As is understood from Table 2, these compounds each have different absorption characteristics from the others so that proper selection of the photo-bleachable compound is essential in the formulation of the

required contrast-enhancing agent and depends on the spectral characteristic of the light used for exposure of the photoresist layer to light. For example, quite satisfactory results can be obtained by using the photo-bleachable compounds of the formulas (V-6), (V-9), (V-10), (VI-3), (VIII-2), (IX-1) and (IX-2) for a light source emitting g-lines, (V-7), (V-8), (V-9), (V-10), (V-11), (VI-2) and (IX-1) for a light source emitting h-lines and (V-1), (V-2), (V-3), (V-4), (V-5), (V-7), (V-8), (V-11), (VI-1), (VI-2), (VII-1) and (VIII-1) for a light source emitting i-lines.

The photo-bleachable compounds represented by the above given general formulas (Ia) and (V) through (IX) are advantageously very stable and do not decompose or change structure : when they are stored over a long period of time. They do not undergo any reaction with other ingredients in the inventive contrast-enhancing agent. Unlike conventional diazo-based contrast-enhancing agents, therefore, the inventive contrast-enhancing agent has a long storage life, without denaturing, even after storage for several years when stored in a dark place.

In addition to the above mentioned stability characteristics, the photo-bleachable compounds used in the inventive contrast-enhancing agent are characteristically soluble in water or a mixture of water and one or more kinds of organic solvents incapable of dissolving the photoresist layer. Accordingly, overcoating of the photoresist layer with the inventive contrast-enhancing agent can be performed without the danger that the underlying photoresist layer is dissolved by the coating solution to cause intermixing of the photoresist composition with the overcoating composition.

When the contrast-enhancing layer is formed from the inventive contrast-enhancing agent comprising the above described photo-bleachable compound and a water-soluble polymeric binder described below, furthermore, the layer can be dissolved in the development treatment of the underlying photoresist layer simultaneously by using an aqueous developer solution so that the development treatment need not be preceded by the removing treatment of the overcoating layer of the contrast-enhancing agent. These advantages can never be obtained by using conventional nitron-based contrast-enhancing agents.

Besides the above described photo-bleachable compound as the component (a), the other essential ingredient in the inventive contrast-enhancing agent is a water-soluble polymeric material as the component (b) to serve as a binder. Various kinds of synthetic and natural water-soluble polymers can be used for the purpose including synthetic and semi-synthetic ones such as poly(vinyl alcohol), partially saponified poly(vinyl acetate), poly(ethylene oxide), poly(acrylic acid), poly(methacrylic acid), polyacrylamide, polymethacrylamide, poly(hydroxyethyl methacrylate), poly(vinylbenzene sulfonic acid), poly(vinyl pyrrolidone), poly(vinyl pyridine), polyethylenimine, and water-soluble cellulose derivatives and natural ones such as pullulan, gelatin, alginic acid, guar gum, gum arabic, tragacanth gum, casein, tamarind pulp, and starch.

The contrast-enhancing agent of the invention is prepared by dissolving the photo-bleachable compound as the component (a) and the water-soluble polymeric material as the component (b) in a solvent which is usually water although a small amount of a water-miscible organic solvent such as alcohols, ketones, esters, or ethers may be added according to need. Furthermore, it is optional, if desired, that the inventive contrast-enhancing agent in the form of an aqueous solution may be admixed with various kinds of known additives such as surface active agents and defoaming agents to improve spreadability, film-formability and other properties.

In the following, the contrast-enhancing agent of the present invention is described in more detail by way of preparations and examples.

Preparation 1.

The photo-bleachable compound represented by the structural formula (II-10) was prepared in the following manner. 6.985 g (0.075 mole) of γ -picoline were dissolved in 20 ml of methyl alcohol and 9.460 g (0.075 mole) of dimethyl sulfate were added dropwise into the solution kept at a temperature of 40 °C or below under agitation. After completion of the dropwise addition of the dimethyl sulfate, the mixture was further agitated for 1 hour to complete the reaction for the conversion of γ -picoline into the form of quaternary salt. The reaction mixture was then admixed with 12.254 g (0.09 mole) of p-anisaldehyde and 1.277 g (0.011 mole) of piperidine followed by heating under reflux for 3 hours. After cooling to room temperature, 20 ml of acetone were added to the reaction mixture so that a crystalline material was precipitated therein. The reaction mixture was filtered to give 20.5 g of the precipitate which could be identified as the compound represented by the formula (II-10). The yield of this product was 81% of the theoretical value.

The above described synthetic procedure was applicable in substantially the same manner excepting replacement of the reactant compounds to the preparation of each of the photo-bleachable compounds (II-1), (II-2), (II-3), (II-4), (II-23), (II-24), (II-25), (II-26), (II-27), (II-29), (II-30), (II-31), (II-32), (II-33), (II-34), (II-35), (II-36), (II-37), (II-38), (II-39), (II-40), (II-41), (II-42), (II-43), (II-47), (II-50), (II-51), (II-52), (II-53), (III-1), (III-2), (III-3), (III-4) and (IV-1).

Preparation 2.

The photo-bleachable compound represented by structural formula (II-44) was prepared in the following manner. 6.782 g (0.025 mole) of 1,4-dimethylquinoline methosulfate obtained from 4-methylquinoline and dimethyl sulfate and 3.603 g (0.0375 mole) of furfural were dissolved in a solvent mixture of 28 ml of isopropyl alcohol and 7 ml of methyl alcohol and the solution was then admixed with 2.26 g of an anion-exchange resin (Amberlite IRA-45, a product by Rohm & Haas Co.) and heated under reflux for 4 hours to effect the reaction. After the end of the above mentioned reaction time, the reaction mixture, while still hot, was filtered to remove

the ion exchange resin and the filtrate was cooled so that precipitates were formed therein. Filtration of the reaction mixture gave 5.14 g of a product which could be identified as the compound represented by the formula (II-44). The yield of this product was 59% of the theoretical value.

The above described synthetic procedure was applicable in substantially the same manner excepting replacement of the reactant compounds to the preparation of each of the photo-bleachable compounds (II-19), (II-20), (II-21), (II-28), (II-45), (II-48) and (II-49).

Preparation 3.

The photo-bleachable compound represented by the structural formula (II-7) was prepared in the following manner. 4.0 g of the compound represented by the formula (II-10) were dissolved in 50 ml of water and 25 ml of concentrated hydrochloric acid were added thereto so that a crystalline material was precipitated in the mixture. The reaction mixture was filtered and the precipitate was washed with acetone and dried to give 2.6 g of a product which could be identified as the compound represented by formula (II-7). The yield of this product was 84% of the theoretical value.

The photo-bleachable compound represented by the structural formula (II-8) was prepared in substantially the same manner as above excepting replacement of the reactant compound.

Preparation 4.

The photo-bleachable compound represented by the structural formula (II-14) was prepared in the following manner. A reaction mixture was prepared by dissolving 6.81 g (0.05 mole) of p-anisaldehyde and 4.66 g (0.05 mole) of γ -picoline in 10.21 g (0.10 mole) of acetic anhydride and the mixture was heated under reflux for 16 hours to effect the reaction. Acetic acid and the unreacted acetic anhydride were then evaporated from the reaction mixture, and the residual reaction mixture was poured into water so that a crystalline material was precipitated therein. The reaction mixture was filtered and the precipitate was washed with water. Recrystallization of the precipitate from a mixture of methyl alcohol and water gave 5.80 g of 4-[2-(4-methoxyphenyl) ethenyl] pyridine, the yield of which was 55% of the theoretical value.

Then, 2.0 g of the thus obtained 4-[2-(4-methoxyphenyl)ethenyl] pyridine were dissolved in 10 ml of dimethylformamide and the solution was admixed with 1.30 g of 2-bromoethyl alcohol and heated at 100 °C for 1 hour to effect the reaction. After cooling to room temperature, 60 ml of acetone were added to the reaction mixture so that a crystalline material was precipitated therein. The reaction mixture was filtered and the precipitate was washed with acetone and dried to give 2.30 g of a product which could be identified to be the compound represented by the formula (II-14). The yield of this product was 72% of the theoretical value.

The above described synthetic procedure was applicable in substantially the same manner excepting replacement of the reactant compounds to the preparation of each of the photo-bleachable compounds (II-5), (II-6), (II-9), (II-11), (II-12), (II-13), (II-15), (II-16), (II-17) and (II-18).

Preparation 5.

4-[2-(2,4-Dimethoxyphenyl)ethenyl] pyridine was prepared in substantially the same manner as in Preparation 4 excepting replacement of p-anisaldehyde with 2,4-dimethoxy benzaldehyde and 2.41 g of this 4-[2-(2,4-dimethoxyphenyl)ethenyl] pyridine were dissolved in a mixture of 1.04 g of concentrated hydrochloric acid and 24.30 g of water. The thus obtained solution was a 10% by weight aqueous solution of the compound of formula (II-22).

An aqueous solution of the photo-bleachable compound of formula (II-46) was prepared in the same manner as above excepting replacement of the reactant compounds.

Preparation 6.

The photo-bleachable compound of the structural formula (V-5) was prepared in the following manner. 10 g of 1,2-xylylene dibromide and 10.6 g of γ -picoline were dissolved in 80 ml of dimethylformamide and the solution was heated at 70 °C for 2 hours to effect the reaction. After cooling to room temperature, the reaction mixture was filtered and the precipitate was washed with acetone to give 15.8 g of a crystalline product.

Then, 10 g of the crystalline material and 22 g of terephthalaldehyde were dissolved in 50 ml of hot methyl alcohol and the solution was admixed with 0.95 g of piperidine and heated at 69 °C for 3 hours to effect the reaction. After the end of the above mentioned reaction time, the reaction mixture, while still hot was filtered to remove insoluble matter and 100 ml of acetone were added to the filtrate, which was kept standing overnight so that precipitate formed therein. The precipitate was collected by filtration, washed with acetone and dried to give 10.6 g of a product which could be identified to be the compound of formula (V-5).

The above described synthetic procedure was applicable in substantially the same manner excepting replacement of the reactant compounds to the preparation of each of the photo-bleachable compounds of (V-1), (V-2), (V-3), (V-4), (V-6), (V-7), (V-8), (V-9), (V-10) and (V-11).

Preparation 7.

The photo-bleachable compound of structural formula (VI-1) was prepared in the following manner. The sodium salt of 4-hydroxybenzaldehyde obtained from 4.88 g of 4-hydroxybenzaldehyde and 1.60 g of sodium hydroxide was dissolved in 15 ml of ethylene glycol monoethyl ether and the solution was admixed with 5.28 g of xylylene dibromide and heated at 120 °C for 2 hours to effect the reaction. After the end of the reaction time,

the reaction mixture was filtered to remove the crystalline precipitates of sodium bromide and 100 ml of benzene were added to the filtrate which was washed successively with water, aqueous alkaline solution and water followed by evaporation of benzene to give 5.26 g of a dialdehyde compound.

5 Then, 1 g of the dialdehyde compound and 1.90 g of a quaternary salt of γ -picoline prepared from γ -picoline and dimethyl sulfate were dissolved in a solvent mixture of 8 ml of benzene and 4 ml of isopropyl alcohol and the solution was admixed with 0.25 g of piperidine and kept at 40 °C under agitation for 2 hours. Thereafter, the reaction mixture was filtered to collect the precipitates formed therein, and the precipitates were purified by recrystallization from ethyl alcohol to give 0.64 g of a product which could be identified to be the compound of formula (VI-1).

10 The photo-bleachable compound expressed of (VI-3) was prepared in substantially the same manner as above excepting replacement of the reactant compounds.

Preparation 8.

15 The photo-bleachable compound represented by the structural formula (VI-2) was prepared in the following manner. 4.00 g of hydroxystilbazole prepared from 4-hydroxybenzaldehyde and γ -picoline and 2.06 g of benzene-1,2-diacetic acid dichloride were dissolved in 40 ml of dimethylformamide and the solution was cooled and admixed with 2.16 g of triethylamine and stood at 20 °C for 2 hours for the reaction to occur. Thereafter, the reaction mixture was filtered to remove the precipitated triethylamine hydrochloride and 150 ml of dichloromethane were added to the filtrate followed by washing with water and then with an aqueous

20 alkaline solution. Evaporation of the solvent gave 3.18 g of distilbazole. A solution of 1.50 g of the distilbazole in 20 ml of dimethylacetamide was admixed with 1.1 g of dimethyl sulfate and the mixture was kept at room temperature under agitation for 4 hours so that a crystalline material was precipitated. The precipitate was collected by filtration and washed with acetone followed by drying to give 2.1 g of a product which could be identified to be the compound expressed by the formula (VI-2).

25 Preparation 9.

The photo-bleachable compound of the structural formula (VII-1) was prepared in substantially the same manner as in Preparation 8 excepting replacement of dimethyl sulfate with 1,3-dibromopropane.

30 Preparation 10.

The photo-bleachable compound expressed by the structural formula (VIII-1) was prepared in the following manner. The potassium salt of 4-hydroxybenzaldehyde obtained from 6.1 g of 4-hydroxybenzaldehyde and 2.80 g of potassium hydroxide and 10.1 g of 1,3-dibromopropane were dissolved in 20 ml of dimethylformamide and the solution was heated at 70 to 80 °C for 2 hours to effect the reaction. The reaction mixture, after

35 completion of the reaction, was admixed with water and extracted with ether. The ether solution obtained by separation was washed with an aqueous alkali solution followed by evaporation of ether. Distillation of the residual mixture under reduced pressure gave 3.5g of the monoether compound. Then, 2.4 g of the monoether compound and 2.1 g of stilbazole prepared from 4-methoxybenzaldehyde and γ -picoline were dissolved in 20 ml of dimethylformamide and the solution was kept at 100 °C for 1.5 hours.

40 After cooling, 150 ml of ethyl acetate were added to the reaction mixture to precipitate a crystalline material. Filtration of the reaction mixture gave 2.9 g of monostilbazolium. 1.36 g of the monostilbazolium and 0.66 g of a quaternary salt prepared from γ -picoline and dimethyl sulfate was reacted in 15 ml of ethyl alcohol containing 0.005 g of piperidine as the catalyst at 60 °C for 3 hours. After completion of the reaction, the reaction mixture was filtered to collect the precipitate, which was washed with

45 ethyl alcohol followed by drying to give 0.62 g of a product which could be identified as the compound of the formula (VIII-1). The photo-bleachable compound expressed by the structural formula (VIII-2) was prepared in substantially the same manner as above excepting replacement of the reactant compounds.

50 Preparation 11.

The photo-bleachable compound of structural formula (IX-1) was prepared in the following manner. 6.31 g of dimethyl sulfate were added dropwise under cooling into a solution prepared by dissolving 4.66 g of γ -picoline in 25 ml of ethyl alcohol. After completion of the dropwise addition of the dimethyl sulfate, the mixture was further agitated at room temperature for 1 hour to complete the reaction for converting the γ -picoline into the

55 form of a quaternary salt. The ethyl alcohol solution of the quaternary salt was then admixed with 4.19 g of terephthalaldehyde and 0.4 g of piperidine followed by heating under reflux for 3 hours. After cooling to room temperature, the reaction mixture was filtered to collect the precipitate. Recrystallization of the precipitate from a mixture of water and methyl alcohol gave 12.60 g of a crystalline product which could be identified as the compound of formula (IX-1).

60 The photo-bleachable compound of structural formula (IX-2) was prepared in just the same manner as above excepting replacement of the reactant compounds.

Example 1.

65 A contrast-enhancing agent in the form of an aqueous solution was prepared by dissolving 2 g of poly(vinyl alcohol) having an average degree of polymerization of 500 and a degree of saponification of 88% and 1.2 g of

the photo-bleachable compound of the structural formula (II-10) obtained in Preparation 1 described above in 25 ml of water. The surface of a glass substrate was coated with the solution and dried at 80 °C for 20 minutes to form a layer of the composition having a thickness of 0.46 μm .

The thus prepared layer of the contrast-enhancing agent on the glass substrate was exposed to ultraviolet radiation of i-line having a wavelength of 365 nm for varied lengths of time. The % transmission of ultraviolet at a wavelength of 365 nm through the layer after exposure is shown by the solid line in FIGURE 1 as a function of the exposure time in seconds.

Example 2.

An aqueous solution prepared by dissolving 2 g of pullulan having an average molecular weight of about 200,000 and 1.2 g of the photo-bleachable compound of structural formula (II-43) in 25 ml of water was uniformly applied to the surface of a glass substrate followed by drying at 80 °C for 20 minutes. The thus obtained film had a thickness of 0.46 μm .

The broken line in FIGURE 1 shows the photo-bleaching characteristics of this contrast-enhancing agent determined in the same manner as in Example 1.

Example 3.

An aqueous solution prepared by dissolving 2 g of poly(vinyl pyrrolidone) having an average molecular weight of about 160,000 and 1.3 g of the photo-bleachable compound of the structural formula (III-1) in 21.7 ml of water and the solution was uniformly applied to the surface of a glass substrate followed by drying to give a film of the composition having a thickness of 0.42 μm on the glass substrate.

The solid line in FIGURE 2 shows the photo-bleaching characteristics of this contrast-enhancing agent determined in the same manner as in Example 1.

Example 4.

An aqueous solution prepared by dissolving 2 g of poly(vinyl alcohol) having an average degree of polymerization of 500 and a degree of saponification of 88% and 1.2 g of the photo-bleachable compound of structural formula (II-31) in 21.5 ml of water was uniformly applied to the surface of a glass substrate followed by drying to give a film having a thickness of 0.45 μm on the glass substrate.

The broken line in FIGURE 2 shows the photo-bleaching characteristics of this contrast-enhancing agent determined in the same manner as in Example 1.

Example 5.

An aqueous solution prepared by dissolving 2 g of poly(vinyl alcohol) having an average degree of polymerization of 500 and a degree of saponification of 88% and 1.5 g of the photo-bleachable compound of structural formula (II-47) in 30 ml of water was uniformly applied to the surface of a glass substrate followed by drying at 80 °C for 20 minutes to give a film having a thickness of 0.45 μm on the glass substrate.

The solid line in FIGURE 3 shows the photo-bleaching characteristics of this contrast-enhancing agent determined in the same manner as in Example 1 except that the light used for exposure and measurement of the transmission had a wavelength of 436 nm.

Example 6.

An aqueous solution prepared by dissolving 0.4 g of poly(vinyl pyrrolidone) having an average molecular weight of about 160,000, 1.4 g of poly(vinyl alcohol) having an average degree of polymerization of 300 and a degree of saponification of 88% and 1.7 g of the photo-bleachable compound of structural formula (II-26) in 21.3 ml of water was uniformly applied to the surface of a glass substrate followed by drying to give a film having a thickness of 0.38 μm on the glass substrate.

The broken line in FIGURE 3 shows the photo-bleaching characteristics of this contrast-enhancing agent determined in the same manner as in Example 5.

It is understood from FIGURES 1 to 3 that the contrast-enhancing agents of the invention exhibit good photo-bleaching characteristics.

Example 7.

A silicon wafer was coated with a positive-working photoresist (OFPR-800, a product of Tokyo Ohka Kogyo Co.) and dried to a thickness of 1.2 μm at 90 °C for 30 minutes.

The photoresist layer was overcoated with the aqueous solution prepared in Example 6 and dried to a thickness of 0.41 μm . The thus coated wafer was exposed to g-line light having a wavelength of 436 nm for varied lengths of exposure time and developed to determine the photosensitivity characteristics. The results are shown in FIGURE 4 by the solid line and broken line for the experiments with and without the overcoating of the contrast-enhancing agent, respectively.

The results in this figure clearly show that the γ value could greatly be improved by using the contrast-enhancing agent of the present invention.

Example 8.

A silicon wafer was coated with the same positive-working photoresist and in the same manner as in Example 7 to give a photoresist layer having a thickness of 1.0 μm and overcoated with an aqueous solution prepared by dissolving 2 g of poly(vinyl alcohol) having an average degree of polymerization of 500 and a degree of saponification of 88% and 1.5 g of the compound of the formula (II-16) prepared in Preparation 4 in 30 ml of water to give an overcoating layer and dried to a thickness of 0.45 μm .

The thus coated wafer was subjected to exposure to g-line light for a line-and-space pattern through a 5:1 wafer stepper (NA 0.35, a product of Nikon Co.) followed by development using a developer solution (NMD-3, a product of Tokyo Ohka Kogyo Co.). The results were that clear resolution was obtained of the line-and-space pattern of 0.8 μm width.

Example 9.

The experimental procedure was substantially the same as in Example 1 except that the coating solution was prepared by dissolving 2 g of the same poly(vinyl alcohol) and 1 g of the photo-bleachable compound of the formula (V-5) in place of the compound of the formula (II-10) in 40 ml of water. The thickness of the thus obtained film was 0.45 μm .

The photo-bleaching characteristics of this coating layer are shown in FIGURE 5.

Example 10.

The experimental procedure was substantially the same as in Example 6 except that the coating solution was prepared by dissolving 3 g of a poly(vinyl alcohol) having an average degree of polymerization of 1400 and a degree of saponification of 88% and 1 g of the photo-bleachable compound of the formula (VIII-2) in place of the compound of the formula (II-26) in 60 ml of water. The thickness of the thus obtained film was 0.57 μm .

The photo-bleaching characteristics of this coating layer are shown in FIGURE 6.

It is understood from FIGURES 5 and 6 that the contrast-enhancing agents of the present invention have good photo-bleaching behavior.

Example 11.

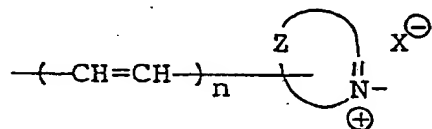
A silicon wafer was coated with a positive-working photoresist composition (Microposit 1400-27, a product of Shipley Co.) followed by drying to form a photoresist layer having a thickness of 0.4 μm . The photoresist layer was overcoated with an aqueous solution prepared by dissolving 2 g of the compound of formula (V-4) and 4 g of pullulan in 80 ml of water followed by drying to form an overcoating layer having a thickness of 0.4 μm .

The thus coated wafer was subjected to exposure to i-line light for a line-and-space pattern through a 10:1 wafer stepper (NA 0.35, a product of Nikon Co.) followed by development using a developer solution (Microposit MF-312, a product of Shipley Co.). The results were that clear resolution was obtained of the line-and-space pattern of 0.5 μm width.

Claims

1. A contrast-enhancing agent for photolithography which comprises:

(a) a photo-bleachable compound having, in its molecule, at least one characteristic structural unit represented by the general formula



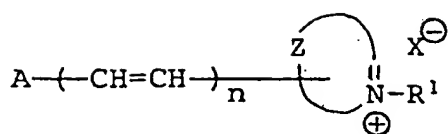
in which Z is a divalent group which forms a heterocyclic aromatic ring structure with the nitrogen atom, X is a monovalent anionic group and n is a positive integer; and

(b) a water-soluble polymer as a binder.

2. A contrast-enhancing agent as claimed in claim 1 wherein n is 1.

3. A contrast-enhancing agent as claimed in claim 1 wherein n is 2.

4. A contrast-enhancing agent as claimed in any one of claims 1 to 3 wherein component (a) is a compound represented by the general formula



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in which A is a substituted or unsubstituted aromatic group and R¹ is a hydrogen atom or a monovalent hydrocarbon group which is an alkyl, alkenyl or aralkyl group, the other groups each being as defined in claim 1.

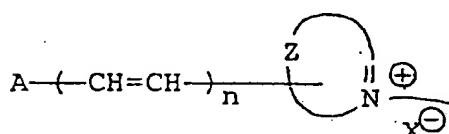
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5. A contrast-enhancing agent as claimed in claim 4 wherein A is a phenyl, naphthyl, furyl, pyrrolyl, thienyl, benzofuryl, benzothienyl, indolyl, pyridyl or quinolyl group.

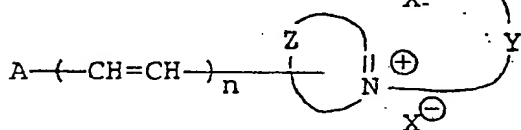
6. A contrast-enhancing agent as claimed in any one of claims 1 to 3 wherein component (a) is a compound having in its molecule, two of the characteristic structural units.

7. A contrast-enhancing agent as claimed in claim 6 wherein the component (a) is a compound represented by one of the general formulae

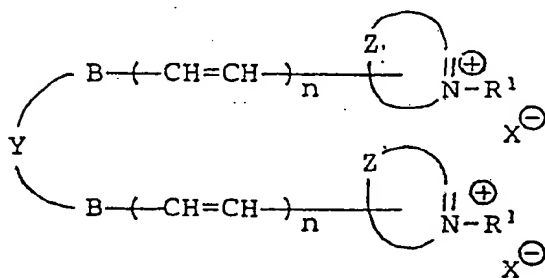
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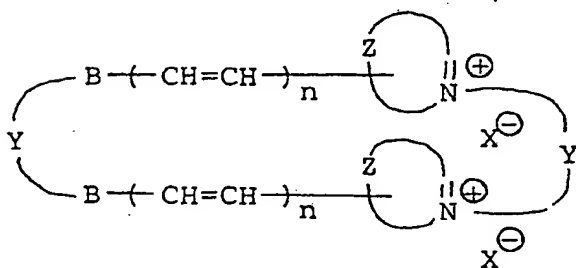


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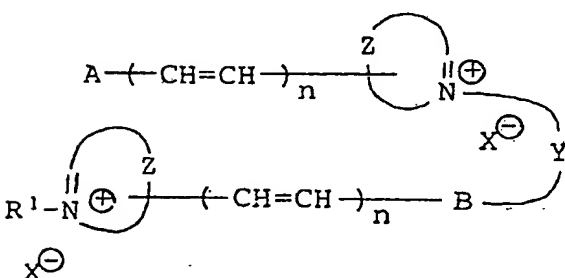
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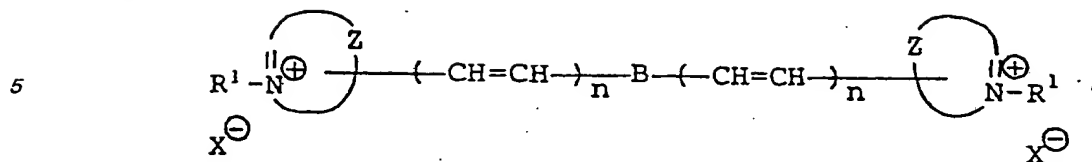


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or



10 In which the symbols, A, Z, R¹, Z and n are each as defined above, Y is a divalent organic group and B is a substituted or unsubstituted divalent aromatic group.

8. A contrast-enhancing agent as claimed in any one of the preceding claims wherein the amount of the water-soluble polymer as component (b) is in the range from 0.5 to 10 parts by weight per part by weight of the photo-bleachable compound as component (a).

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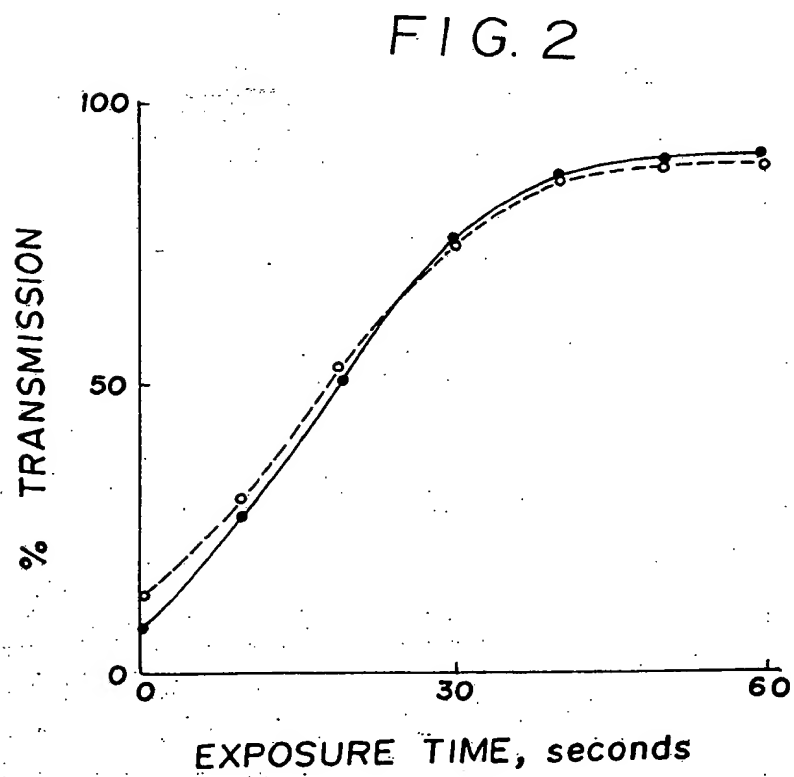
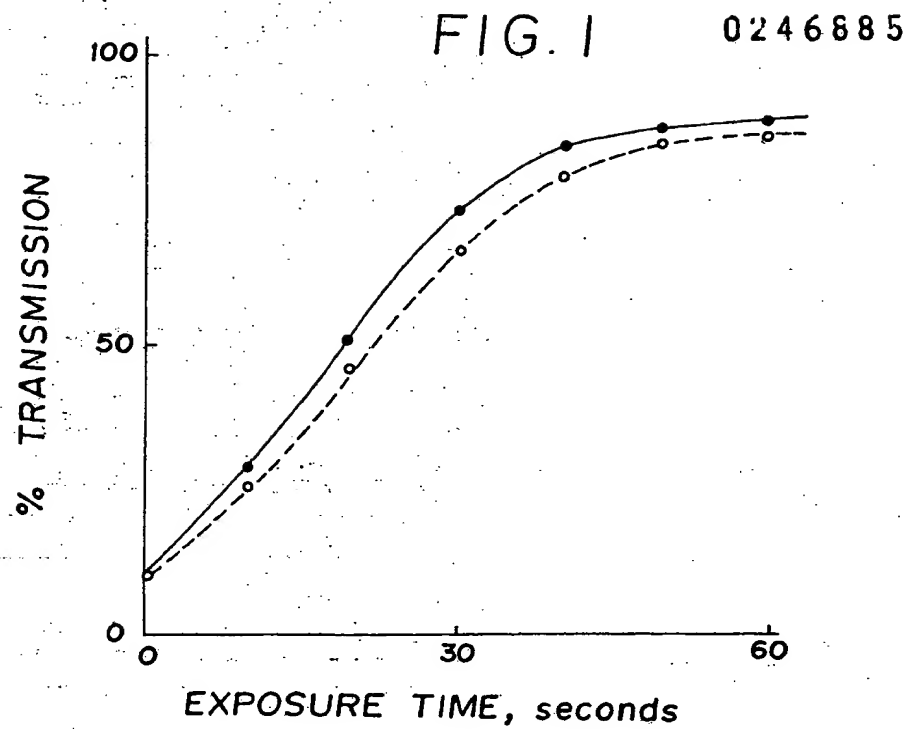


FIG. 3

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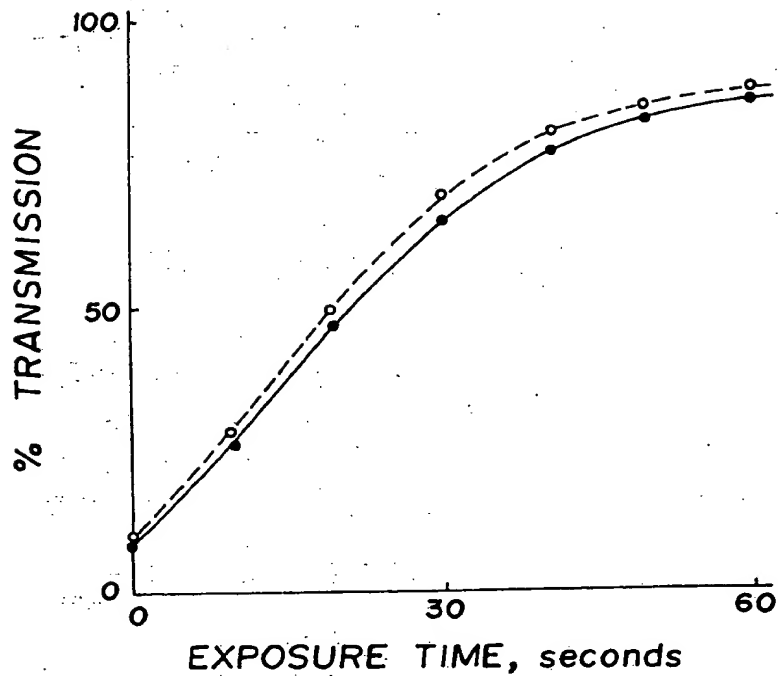


FIG. 4

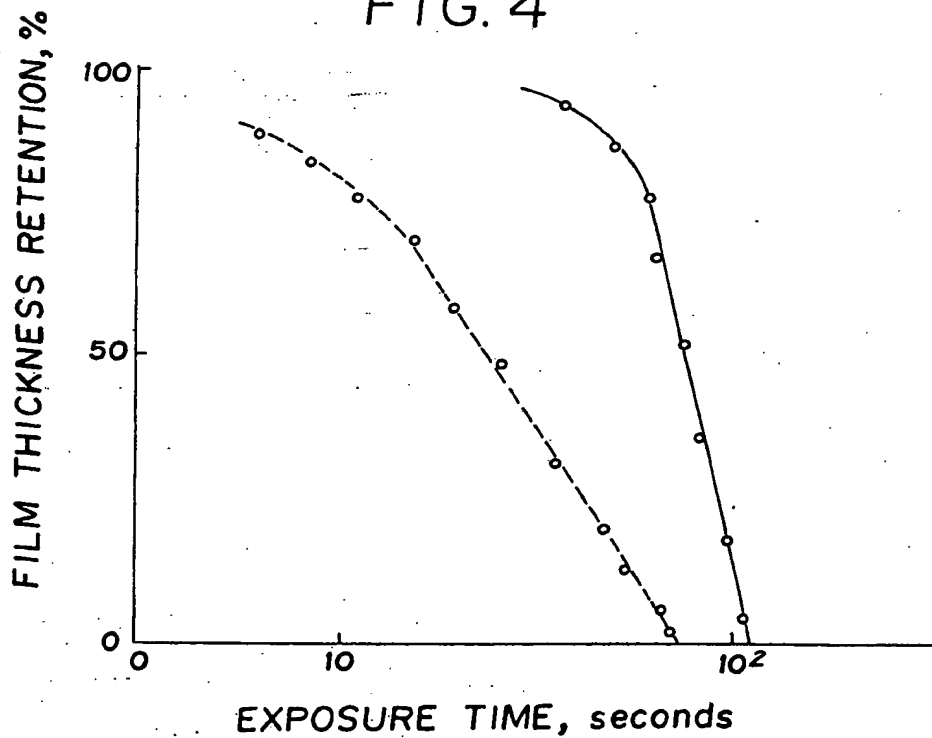


FIG.5

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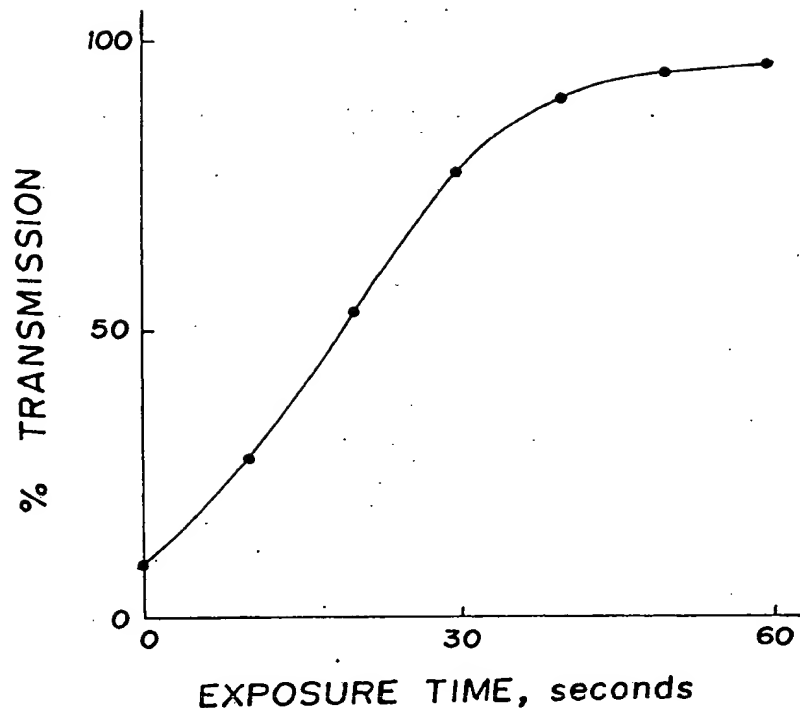
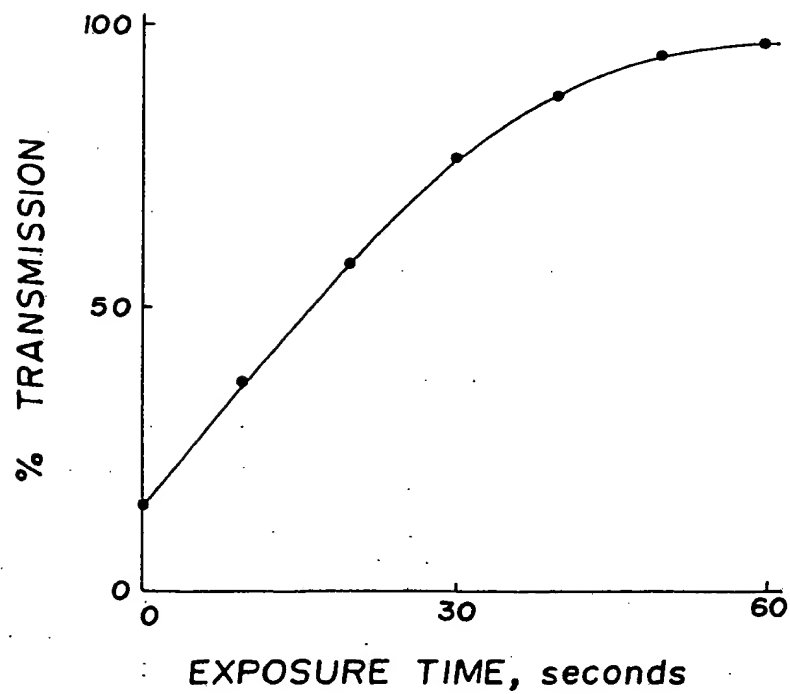


FIG.6





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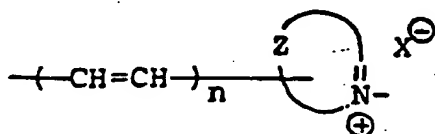
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84 **A contrast-enhancing agent for photolithography.**

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Application Number

EP 87 30 4498

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	DE-A-2 216 500 (AGFA-GEVAERT AG) * Page 7, formula 8; page 16, lines 1-23; claims *	1-5,8	G 03 F 7/02
Y	US-A-4 111 699 (KRUEGER) * Columns 1-3; column 4, lines 1-63; column 8, lines 16-52; column 9, lines 36-57; claims *	1-5,8	
Y	US-A-3 996 215 (KOBAYASHI et al.) * Columns 1-5,29-66 *	1-5	
D,Y	EP-A-0 110 165 (GENERAL ELECTRIC CO.) * Claims *	1,8	
A	MICROELECTRONIC ENGINEERING, vol. 3, no. 1-4, December 1985, pages 321-328, Elsevier Science Publishers B.V. (North-Holland), Amsterdam, NL; M. BOLSEN: "To dye or not to dye - some aspects of today's resist technology" * Whole document *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			G 03 F 7/00 G 03 C 1/00 G 03 C 7/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04-03-1988	Examiner MAGRIZOS S.
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